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ORIGINAL RESEARCH

A modest method of synthesis Cu- based metal-organic frameworks using benzene dicarbocxylate as a ligan for promising candidate of flue gas CO_2 adsorption

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Abstract. Metal organic framework (MOF) is one of extraordinary materials in many technical field applications. One of them is as CO_2 gas adsorbent. We studied, synthesized, and characterized Copper-based material, known as Metal organic frameworks (MOFs), using a solvothermal-based modification method. Copper salt (Cu $(NO_3)_2$. $3H_2O$) and benzene dicarboxylic acid (H_2BDC) were mixed and then heated in an oven at 120°C, to produce low impurities, small pore and uniform particle size of materials called CuBDC. Infrared spectroscopy and XRD data confirmed the formation of CuBDC. Furthermore, the result showed that CuBDC frameworks have good thermal stability up to 330°C. Thereafter SEM picture showed random, layered, and asymmetrical corners structure which is typical of triclinic crystal system. Lastly, specific surface areas and the porosity were analyzed using The Brunauer-Emmett-Teller (BET) method. It recorded 485 $m^2.g^{-1}$ of surface area while average pore volume and average pore size are 0.16 $cm^3.g^{-1}$ and 5.9 Å respectively.

Keywords: Metal Organic Framework, CCS, CuBDC, adsorbent

INTRODUCTION

Research on CO_2 gas adsorbent materials continue to grow rapidly in line with the increasing volume of CO_2 gas formed because of industrial activities. Increasing concerns about environmental damage and disruption to human health due to the chain effect of these gas in large quantities bring more the need for separation technology or gas purification for specific applications immediately. One of the old technologies for gas separation or purification is using membrane. The separation or purification technology using a membrane is relatively more advantageous because it does not require phase transformation. This is because all the separation methods except the membrane method involve changing the phase from gas to liquid or solid state. In addition, the separation technique using the membrane method requires equipment that is relatively simple, compact, easy to control and operate and easy to increase productivity. Currently membrane technology gives good results when used for the purification of natural gas with moderate gas volume flows. However, if the gas volume flow is large, the membrane technology cannot compete with the amine absorption method. Separation of CO_2 is carried out using liquid amines, where CO_2 gas reacts with the amines to form carbamates as shown in the reaction below:

$$R - NH_2 + H_2O + CO_2 \rightleftharpoons R - NH_3^+HCO_3^-$$

The reaction of CO_2 gas with amines is an alternating reaction, where CO_2 can be released again by heating to a temperature of 150 ° C. However, the use of liquid amines as a CO_2 separator in natural gas has several drawbacks, namely, CO_2 contamination makes amines corrosive, volatile and unstable over time. The amine adsorption method is known to be reliable, high productivity, but with the above limitations causing high operational costs / expensive, and complex technical operations because it involves phase changes.

The discovery of new porous materials called Metal-Organic Frameworks (MOFs) in the end of 20th century provided new alternatives and perspectives in CO_2 gas separation or adsorption technology to be more effective and efficient than previous gas adsorption

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technologies. Metal-Organic Framework (MOFs) is a porous crystalline material which is formed through a coordination bond between the metal ion cluster as the center and the organic ligand as a linker which produces a framework [1]. The framework on MOFs is called secondary building units (SBUs) and has permanent porosity [2]. Figure 1 describes the mechanism for establishing SBUs. The uniqueness of MOFs includes a large surface area, high thermal resistance, and a modified structure. These properties make MOFs a superior candidate for application in various fields, including catalysts, adsorbents, gas separators, sensors, photoluminescent, fuel cells, batteries, and drug delivery.

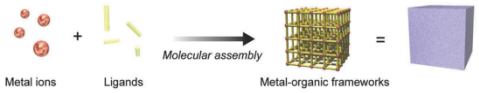

Figure 1. The mechanism of secondary building units (SBUs) formation.

various types of other metal-based MOFs have been found, such as MOF-2 (Zn), IRMOF-3 (Zn), UiO-66 (Zr), and MIL-53 (Al). Zinc (Zn) based MOF-5 was first synthesized by Li and his colleagues in 1999 [3]. These MOFs are composed of Zn metal clusters with $Zn_4O(CO_2)_6$ SBUs linked by benzene-1,4-dicarboxylate (BDC) ligands [4]. Another type of Zn-based MOFs is MOF-2 which has SBUs $Zn_2(CO_2)_4(H_2O)_2$. MOF-2 was synthesized by solvothermal technique at room temperature for 24 hours [5]. MOF-2 has metal ions with unsaturated coordination, or it is called open metal site (OMS) which can increase the adsorption selectivity of MOFs against CO_2 because of its high cationic charge density [6]. SBUs and the structure of the MOF-5 are shown in Figure 2.2.

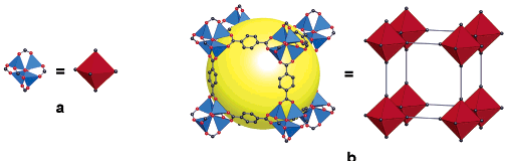

Figure 2. The secondary building units for (a) octahedral $Zn_4O(CO_2)_6$ and the structure of MOF-5 [2].

Research related to adsorbent materials, separation, or purification of CO_2 gas has been stagnating for decades. This is inseparable from the stagnation of the type of material involved in the process. Amine absorption methods that are expensive, complex, and not environmentally friendly are still the main choice because nothing has surpassed them in terms of productivity. The discovery of MOFs is good news because of their potential character and can be easily composited to make membranes. However, this MOFs hybrid membrane technology is still relatively new, so there are still many factors that need to be studied and optimized. There are tens of thousands of types of MOFs, so a suitable type must be selected to make MOFs hybrid membranes and can work well as CO_2 gas adsorbent materials. The flue gas separation method using membranes has advantages over other methods related to energy saving and technological simplicity in gas separation applications. However, membranes also have challenges that must be resolved related to the less-than-optimal membrane method for gas separation processes with large gas volume flows.

In the last two decades, copper (II) benzene dicarboxylates (CuBDC) have received considerable attention as attractive materials for adsorbing gases. Mori et. al. reported the first CuBDC with a large surface area [7]. They synthesized CuBDC solid in methanol using copper (II) format as precursor of Cu. Thereafter Seki et. al. synthesized composite material between CuBDC and polymer for gas adsorption [8]. Furthermore, other studies of adsorbent porous copper (II) dicarboxylate have also been reported by Carson, Xin, and co-workers [9, 10]. They developed a new solvent-exchange technique for getting large surface area and large pore size. Above CuBDC materials are synthesized based on solvothermal method. Those methods require more than 24 hours in synthesis and need complicated procedures, and instruments to get CuBDC powder with large surface area and pore size. Unfortunately, not all laboratories can access and have these tools.

In this research, we synthesized porous CuBDC using a modification method which was simple, relatively fast, and easy to do. This method can be used for synthesizing majority types of MOFs. By using this method, we expect getting relatively large surface area, and suitable pore volume and pore size for adsorbing CO_2 from flue gas.

METHODOLOGY

Synthesis

All chemicals were gained commercially and used without additional purification. Copper nitrate trihydrate ($Cu(NO_3)_2 . 3 H_2O$) (Sigma Aldrich), benzene-1,4-dicarboxylate (H_2BDC) (sigma Aldrich), N, N'-dimethylformamide (DMF) (99% Merck), and methanol (sigma Aldrich). The procedure of synthesizing CuBDC reported in the literature [7] was modified in term of Copper salt, solvent, and

activation procedures. The details are defined as follows; copper nitrate trihydrate (2.41 g) and benzene-1,4-dicarboxylate (1.66 g) were dissolved in 200 mL DMF. After stirring and the mixture becoming homogeneous, this solution was placed in a closed transparent bottle and then located in an oven at 120°C for 24 h. After the reaction, the bottle was taken out of the oven and cooled down to room temperature. The powders were separated from the solvent and were washed thoroughly with DMF one time, then were washed with methanol two times. After repeated washing and centrifugation process, the prepared CuBDC powders were dried in an oven for 3 hours at 80°C. After doing those process, the yield percentage is 70 %. For getting large surface area, dried CuBDC powder must be activated in a furnace at 220° for 24hours.

Characterization

Infrared spectrum of absorption or emission of the samples were recorded with *NICOLET iS5* FT-IR spectrophotometer by using ATR windows.

The pattern of Powder X-ray diffraction (XRD) of samples was recorded using a *BTX III Benchtop XRD Analyzer* with Co-Kα as radiation source (k = 1.789 Å). The instrument was operated at 30 kV, 10 W and at a scanning step of 0.1° in the 2θ range 5° - 55°.

Thermal properties of sample were analyzed using *Thermogravimetry Analyzer SDT 650* under 150 mL/min N_2 stream with heating rate of 10°C/min from room temperature to 500°C.

The morphological surface of sample was characterized using *Phenom Pro-X brand* scanning electron microscope (SEM). Carbon tape was used as a sample holder.

Specific surface areas and the porosity were analyzed with *Micrometrics TriStar II* gas sorption and porosimeter device using nitrogen gas with low pressure at 77 K. Before the measurements, 0.2 g of sample was heated at 150°C under vacuum for 6 h.

RESULTS AND DISCUSSION

We have used DMF at high temperature to carry out the reaction of CuBDC formation shown in Equation 1.

$$Cu(NO_3)_2.3H_2O + C_6H_4(COOH)_2 \xrightarrow[120^{\circ}C,24h]{DMF,air,} Cu[C_4H_6(COO)_2](DMF) + 2HNO_3 \quad (1)$$

Physical and chemical properties of CuBDC are characterized using instruments as describe in the following explanation.

FTIR Spectroscopy

The interaction of copper ions and H_2BDC ligands in the solvent triggers the formation of covalent coordination bonds between copper ions and oxygen atoms [11]. As shown in Figure 3, the wave numbers of 1673 cm^{-1} and 1281 cm^{-1} indicate the presence of C=O and C-O groups from H_2BDC respectively. The stretching of C=O absorption band seems to be shifted to 1662 cm^{-1} for a molecule that is attached to the Cu ions. Meanwhile stretching of C-O vibration has also shifted its absorption band to 1297 cm^{-1} after coordinating with center of Cu ions. C=O and C-O groups from terephthalic acid interact with the copper ions and convert them into a single C-O→Cu bond [9]. Finally, absorption band of Cu-O stretching was detected at wave number of 751 cm^{-1} [12].

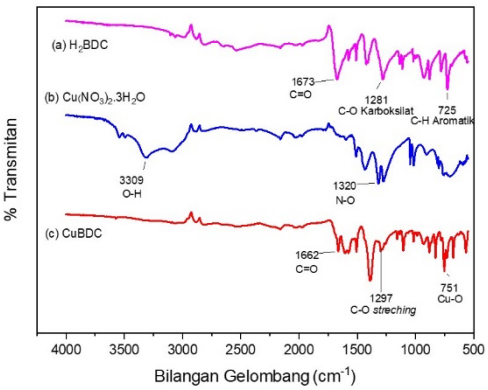

Figure 3. FTIR spectrums of: (a) benzene-1,4-dicarboxylate acid (H_2BDC), (b) copper nitrate, (c) Synthesized CuBDC

From FTIR spectra, one can see that different functional group, which having free electron pair, can coordinate to the Cu atom with different interaction. Selectivity to coordinate specific functional group over another would make MOFs as potential candidates for the application in molecular sieving or gas separation [13]. It also displays that the structure of MOFs can be modified using different solvents which will change the chemical properties and bond strength between adjacent of MOFs layers [14, 15].

From FTIR data, we assume that the target materials have been synthesize successfully.

X-Rays Diffraction

The XRD pattern of CuBDC solids in this study showed typical peaks at 2θ = 10.1; 12.0; 13.5; 17.1; 20.4; 24.8; and 34.0° which has good

agreement with previous study [11]. Based on figure 4, the structure of synthesized CuBDC have confirmed.

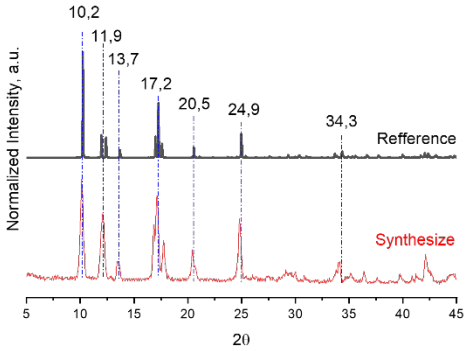

Figure 4. XRD patterns: (black) reference [9], (red) Synthesized CuBDC.

Some of the CuBDC diffraction peaks give some information regarding to the lattice crystalline structure. CuBDC has crystal system triclinic with unit-cell parameters are shown in table 1.

Table 1. Unit-cell parameters of CuBDC [9].

CuBDC					
a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)
5.25	9.67	10.77	90.29	91.06	92.41

The average crystallite size of CuBDC in this study is 22.18 nm, which was calculated by using *Scherrer* equation. This size was smaller than the previous studies have been reported [16, 17]. Meanwhile, the total crystallinity of synthesized CuBDC was 91 % which is relatively similar with what have been reported by others [18, 19].

Thermal Gravimetric Analysis (TGA)

As can be seen in Figure 5, there was several mass losses during the thermal gravimetry analysis (TGA) of the synthesized CuBDC. The first mass loss starts at 160°C which corresponding to DMF evaporation from CuBDC surfaces. This profile is supported by boiling point of DMF which is in the range of 152-154°C. After that, all DMF, which trapped in the CuBDC pores, has been removed at 278°C. These results are in good agreement with the previous study [11]. Finally, the mass loss in this temperature range is 23% of the total mass of the sample.

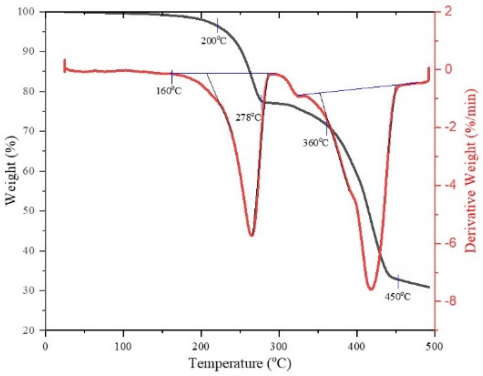

Figure 5. Thermogram of synthesized CuBDC

The next significant mass loss occurred in the range of 330 – 450°C by 47%. This indicates that the MOFs begins collapse at that temperature. At these range of temperature, CuBDC retains its molecular formula but loses its microporous properties. This finding is consistent with what others have reported [20].

At temperature higher than 450° C, CuBDC framework could not retain its crystal structure because the bond between the copper ion and organic molecule (H_2BDC) was not stable. copper ions were reduced to form Cu, Cu_2O or CuO while organic molecules were decomposed to form CO_2, and CO [20, 21]. At these range of temperature, the residual mass is less than 30 %.

Scanning Electron Microscopy (SEM)

Based on observations using SEM, surface morphology of CuBDC is shown in Figure 6. Through this image, it is known that the CuBDC surface structure is random, layered, and forms asymmetrical corners. This condition is in line with the results obtained in previous studies [9].

Mori et al. suggests that the layers on the surface of material are caused by the interaction of copper ions surrounded by oxygen atoms (linker) and agglomerate to form a one-dimensional pore and overlap perpendicularly as shown in Figure 7 [22].

Nitrogen Isotherm adsorption

Isothermal curve of powder CuBDC is shown in figure 8. According to IUPAC classification, the type of isotherm curve of CuBDC shows type I which indicates the occurrence of gas physisorption on microporous material. By definition, a microporous material is a material containing pores with diameter less than 20 Å [13].

Figure 6. Morphological picture of synthesized CuBDC.

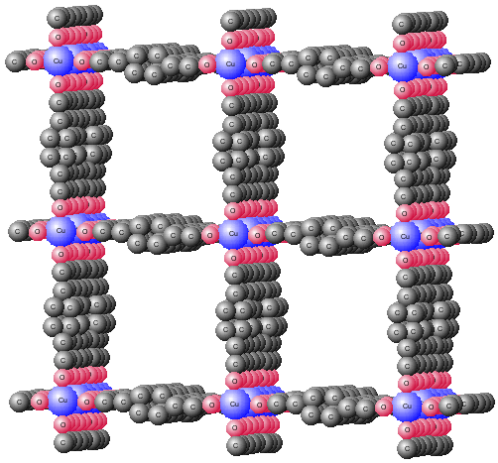

Figure 7. Plated Structure of CuBDC. Copper ions (blue), Oxygen atom (red).

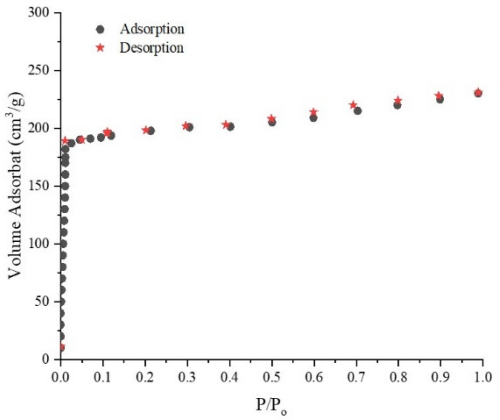

Figure 8. The BET isotherm curve of CuBDC

The curve on figure 8 shows little differences between adsorption and desorption profile which indicates reversible gas storage. Furthermore, synthesized CuBDC has 485 $m^2 g^{-1}$, 0,16 $cm^3 g^{-1}$, and 5,9 Å for BET surface area, pores of volume, and average pore size correspondingly.

Compared with similar work using different method in synthesizing CuBDC, our work has moderate result for all parameters as listed in table 2.

Table 2. Comparation between different synthesis of CuBDC.

System	BET surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Pore size (Å)
In MeOH [7]	545	0.22	6
In DMF [23]	345	0.14	5
In DMF/CHCL [10]	241	-	8.5
In DMF/MeOH [9]	903	0.3	5.8
This Study In DMF	485	0.16	5.9

Uptake CO_2 measurement is not conducted yet because difficulties of access on such an instrument. However, pore size of Synthesized CuBDC is bigger than kinetic diameters of CO_2 (3.3 Å). Therefore, synthesized CuBDC has potential to be used as CO_2 adsorbent.

CONCLUSION

Synthesis of Copper-organic frameworks with benzene-1,4-dicarboxylate (H_2BDC) as linkers have been performed using solvothermal-based modification method. This method is simple, easy and can be used for synthesizing majority types of MOFs. Based on the obtained data from XRD, FTIR, and BET, it can be concluded that CuBDC solid is successfully formed with relatively high of crystallinity degree (91 %), and large surface area (485 $m^2 g^{-1}$). CuBDC crystal structure is not dominated by one type of structure, but its crystal system is triclinic [9]. Synthesized CuBDC has average pore size 5.9 Å and this number is larger than kinetic diameters of CO_2. Hence this MOFs can be applied as CO_2 adsorbent both in low and high pressure.

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